Redox Reactions of Technetium Induced by Bremsstrahlung and Ultrasonic Irradiation : Formation and Dissolution of Tc(IV)02・nH20 Nanoparticles

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論　文　目　次

論 文 内 容 要 旨

Chapter 1. Introduction

Technetium-99 is a long-lived fission product with a half-life of 2.11 x 10^5 y produced in appreciable amounts in nuclear fuel. Because of its long half life, the migration of ^{99}Tc in the environment is of great importance from a viewpoint of high level radioactive waste disposal in deep underground. Another point to be stressed is a radiolytic effect on the migration of radionuclides from the spent nuclear fuel contacted with groundwater, because a high dose is anticipated to its surroundings for a long period of time. Radiolysis of water gives some reactive species such as hydrated electrons (e_{aq}^-), OH and H radicals that are strong redox agents. Those species will induce redox reactions on Tc in the fuel under radiolytic circumstances.

It should also be mentioned that OH and H radicals generated in water radiolysis are also produced in water sonolysis. Therefore the chemical effects of ionizing radiation are often similar to those of ultrasound in aqueous solution. Those effects on redox reactions of Tc are studied in this research.

Chapter 2. Experimental

Bremsstrahlung irradiation was carried out in the Laboratory of Nuclear Science Tohoku University. Electrons from a linear accelerator were coverted to bremsstrahlung by hitting to a platinum converter. The electrons were removed by a sweep magnet. Samples for the irradiation were prepared from aqueous solutions of pertechnetate in the concentration range of 1.0 E-6 − 2.9 E-4 M. The reaction atmosphere was under O_2, N_2O, H_2, Ar and air. The Ar-saturated solutions were prepared with the following treatments: with and without 0.2 M *t*-butyl alcohol, pH 1−7, and in the presence and absence of $TcO_2 \cdot nH_2O$ colloids. The target solutions for ultrasonic irradiation were prepared by the same procedures used previously in the bremsstrahlung irradiation and hydrosols of $TcO_2 \cdot nH_2O$ colloid were also prepared for sonolytic dissolution experiments. Ultrasonic irradiation was conducted by using

ultrasonic transducer and generator.

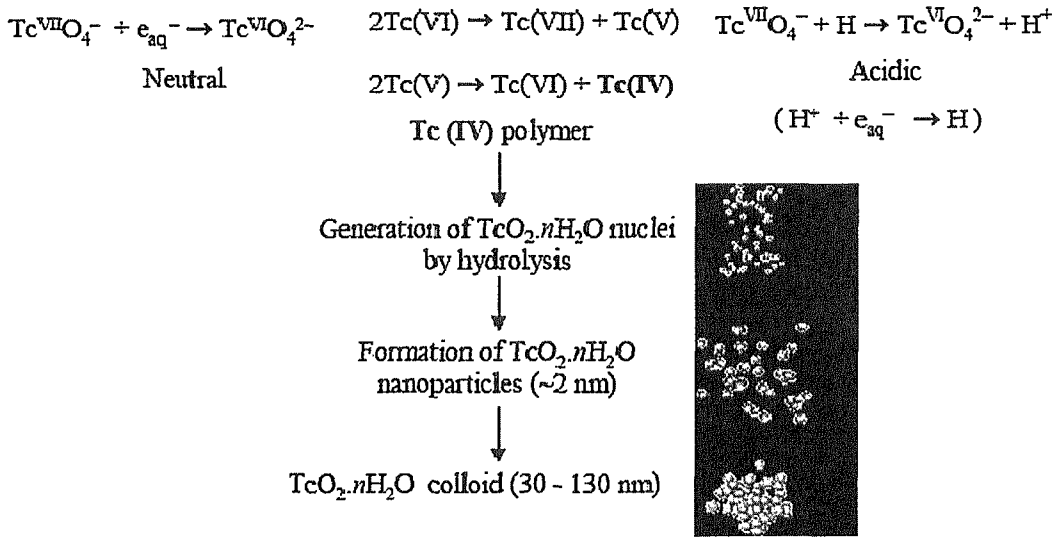
Chapter 3. Formation of $Tc(IV)O_2 \cdot nH_2O$ nanoparticles by bremsstrahlung irradiation

Technetium(IV) oxide colloids, as an aggregate of nanoparticles of 2 nm in diameter, were produced by bremsstrahlung irradiation of aqueous solutions of TcO_4^-. The colloid was characterized in terms of the charge, size, crystalline structure, composition and hydration number (Table 1). The yield of colloids sharply increased with an increase of absorbed dose in the solutions deaerated by Ar- or H_2-bubbling before irradiation, but it was strongly suppressed in the solutions saturated with oxygen (O_2) or nitrous oxide (N_2O). Both O_2 and N_2O are known as an effective scavenger for hydrated electron (e_{aq}^-), a dominant reductant produced by radiolysis of water. The reduction of TcO_4^- to afford $TcO_2 \cdot nH_2O$ colloids proceeded mainly through the processes involving a bimolecular reaction of TcO_4^- with e_{aq}^- (Scheme 1) followed by the successive disproportionation reactions of Tc(VI) and Tc(V).

Table 1 Characterization of the $TcO_2 \cdot nH_2O$ colloids

Properties	Results
Chemical composition	$TcO_2 \cdot nH_2O$, $n \sim 3$
Size	30−130 nm; formed as an aggregate of nanoparticles of 2 nm
Crystalline structure	Amorphous
Point of Zero Charge	pH 1.5−3

Soluble Tc(IV) polymeric species, a precursor of $TcO_2 \cdot nH_2O$ colloids, were formed by the irradiation of acidic solution of TcO_4^-. The result indicates that hydrogen radicals effectively reduce $Tc^{VII}O_4^-$ to form Tc(IV) polymer species, since hydrated electrons are converted to hydrogen radicals in acidic water. Because the rate constant of both reactions $H^+ + e_{aq}^-$ and $TcO_4^- + e_{aq}^-$ is in the same order of magnitude, those two reactions should compete depending on the concentration of H^+ and TcO_4^-. When the concentration of TcO_4^- is 0.1 mM at pH lower than 3, hydrated electrons dominantly react with protons to generate hydrogen radicals. Thus, in the acidic condition, the reduction of TcO_4^- should be initiated by a bimolecular reaction with hydrogen radicals (Scheme 1).



Scheme 1. Formation processes of $TcO_2 \cdot nH_2O$ colloids by radiolysis.

Simulation of the consumption of TcO_4^- ions through the processes in both neutral and acidic solution by using software FACSMILE (AEA Technology) revealed that the experimental values were reproduced by the simulation, supporting the above scenario (Scheme 1) for the reduction of TcO_4^- ions to produce $TcO_2 \cdot nH_2O$ colloids.

Chapter 4. Dissolution of $Tc(IV)O_2 \cdot nH_2O$ nanoparticles by ultrasonic irradiation

It was found that the $TcO_2 \cdot nH_2O$ colloids dispersed in an aqueous solution (under Ar or He atmosphere) were completely dissolved by ultrasonic irradiation (200 kHz, 200 W), and TcO_4^- was eventually produced. The production of TcO_4^- was considerably suppressed in the presence of *t*-butyl alcohol (an effective scavenger of OH radicals), indicating that Tc was oxidized by OH radicals produced in cavitation bubbles. The formation rate of TcO_4^- under He atmosphere was slower than that under Ar atmosphere (Table 2). This can be attributed to a difference of the effective maximum temperature in the collapsing bubbles. Because the thermal conductivity of He is larger than that of Ar, thermal transport effectively occurs from the bubbles to the surrounding liquid. Thus, cavitation bubbles filled with He should be cooler than those filled with Ar, resulting in the slower OH formation rate.

Tabel 2 Effect of noble gases on the formation rate of TcO_4^- in samples and OH radicals in pure water

Saturating gas	TcO_4^- formation rate μ M min^{-1}	OH formation rate μ M min^{-1}	Thermal conductivity (s), mW m^{-1} K^{-1} (300 K)	Polytropic index, γ = Cp/Cv (25 °C)
He	3.30	11.6	156.7	1.65
Ar	10.1	28.1	17.90	1.66

Chapter 5. Conclusions

It was found that $TcO_2 \cdot nH_2O$ colloid was radiolytically produced by bremsstrahlung irradiation of aqueous solutions of TcO_4^-. The reduction of $Tc(VII)O_4^-$ to afford $Tc(IV)O_2 \cdot nH_2O$ colloid was triggered by hydrated electrons (e_{aq}^-) in the neutral solutions, while in the acidic solution the reduction was initiated by H radicals. The size of the colloids was in the range of 30 − 130 nm. They were formed as an aggregate of a number of nanoparticles of 2 nm in diameter. The colloids were stable in the solution for a long time (at least 1 year). Its structure is amorphous and the point of zero charge lies in the pH of 1.5 − 3. The precursor of the colloids was discovered as a soluble and stable species in the acidic solution.

It is noteworthy that the formation of $TcO_2 \cdot nH_2O$ colloids by radiolysis should be emphasized from the viewpoint of environmental migration of technetium in groundwater after disposal of high-level radioactive wastes. Since the rate constant of the $e_{aq}^- + TcO_4^-$ reaction is three orders of magnitude larger than the $H + TcO_4^-$ reaction, the reduction of TcO_4^- by e_{aq}^- is dominant in neutral water such as groundwater.

On the other hand, TcO_4^- was formed by ultrasonic irradiation of turbid solutions of $TcO_2 \cdot nH_2O$ colloids. The oxidation of $Tc(IV)O_2 \cdot nH_2O$ colloids to $Tc(VII)O_4^-$ solutions was induced by OH radicals. The formation rate of TcO_4^- under He atmosphere was slower than that under Ar atmosphere. The difference can be explained based on the difference of the effective maximum temperature in the collapsing bubbles under both gases.

論文審査の結果の要旨

本論文は，放射性元素テクネチウムを対象とし，放射線照射および超音波照射によりそれぞれ引き起こされる酸化還元反応を調べたユニークな内容を含むが，それだけではなく，放射線照射により酸化テクネチウム(IV)水和物($Tc(IV)O_2 \cdot nH_2O$)のナノ粒子生成を認めたことや，ナノ粒子が超音波照射により溶解していくなどの新たな現象を見出し，その反応機構を明らかにした点で高い学術的価値を有している。

第１章では本論文の研究背景と研究目的を記述している。第２章は実験に関する項目をまとめている。第３章では，過テクネチウム酸イオン (TcO_4^-)を含む水溶液を制動放射線照射した際に，$Tc(IV)O_2 \cdot nH_2O$のコロイド粒子(30-130 nm)が生成することを記述している。この粒子はナノ粒子(2 nm)の集合体であることがわかったほか，組成や構造，水溶液中における安定性，粒子の電荷等の無機化学的諸性質を明らかにした。また，TcO_4^-の還元反応では，水の放射線分解で生成する水和電子が重要な役割を果たしていることを明快に示したほか，生成するナノ粒子の前駆体が酸性水溶液中で安定化されることも明らかにした。さらに還元反応機構を提案し，計算値と実験値との整合性よりその妥当性を確認している。第４章では，超音波照射によるテクネチウムの酸化反応を主に記述している。テクネチウムの還元反応が進む放射線照射とは異なり，超音波照射では酸化反応が進行しやすいことが判明した。水溶液中の$Tc(IV)O_2 \cdot nH_2O$ナノ粒子がわずか30分程度の照射で溶解し，TcO_4^-が定量的に生成することを見い出した。これは超音波照射により引き起こされるキャビテーション現象のためで，高温高圧状態のバブル内で生成するOHラジカルがテクネチウム(IV)の酸化に重要な役割を果たしていることがわかった。さらに，雰囲気の違いによるテクネチウムの酸化速度を比較したところ，Ar雰囲気下の方がHe雰囲気下に比べて速度が約3倍大きかった。これはHeの熱伝導性がArよりもはるかに高いことに起因し，生成するバブルの温度が結果的に低下するので，OHラジカルの生成速度にも3倍の開きが生じることを明らかにした。

以上のように，著者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。よって Muhammad Zakir 提出の論文は博士（理学）の学位論文として合格と認める。